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(54) **POLYISOCYANATES A TERMINAISON OH ET A FONCTION
URETDIONE, PROCEDE DE PREPARATION ET
UTILISATION**

(54) **OH-TERMINATED, URETDIONE-FUNCTIONAL
POLYISOCYANATES, A PROCESS FOR THEIR
PREPARATION AND THEIR USE**

(57) Polyisocyanates à fonctions hydroxyle et uretdione comprenant essentiellement A) de 55 à 86 % en poids d'uretdione B) de 1,5 à 15 % en poids de polyol portant > 3 groupes hydroxyle et C) de 7,0 à 30 % en poids de diol, les polyisocyanates portant des groupes hydroxyle terminaux et ayant une fonctionnalité de > 2 à < 3, des masses molaires variant entre 1 600 et 15 000, et une teneur en isocyanate libre < 0,5 % en poids.

(57) Hydroxyl- and uretdione-functional polyisocyanates essentially comprising A) from 55 to 86% by weight of uretdione B) from 1.5 to 15% by weight of polyol with > 3 hydroxyl groups and C) from 7.0 to 30% by weight of diol the polyisocyanates carrying terminal hydroxyl groups and having a functionality of > 2 to < 3, molar masses of between 1600 and 15,000, and a free isocyanate content of < 0.5% by weight.



Abstract:

5 OH-terminated, uretdione-functional polyisocyanates, a process for
their preparation, and their use

Hydroxyl- and uretdione-functional polyisocyanates essentially comprising

- 10 A) from 55 to 86% by weight of uretdione
B) from 1.5 to 15% by weight of polyol with ≥ 3 hydroxyl groups and
C) from 7.0 to 30% by weight of diol

the polyisocyanates carrying terminal hydroxyl groups and having a
functionality of > 2 to < 3 , molar masses of between 1600 and 15,000, and a
15 free isocyanate content of $< 0.5\%$ by weight.

OH-terminated, uretdione-functional polyisocyanates, a process for their preparation, and their use

5 The invention relates to OH-terminated, uretdione-functional polyisocyanates having a functionality of > 2 to < 3 , to a process for their preparation, and to their use for preparing polyurethane (PU) polymers, especially PU coating systems which are free from elimination products, very preferably of transparent and pigmented PU powder coating systems, and to the colorfast and weather-stable PU coatings produced accordingly.

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Polyisocyanates for use in polyurethane powder coatings, containing uretdione groups, are known in particular from DE-A-30 30 554. Polyisocyanates of that kind, however, have only two terminal, partly or completely blocked isocyanate groups, and are strictly linear in structure. As
15 is evident from EP-A 254 152 (page 2, column 1, line 63 to end of sentence), this fact is a great disadvantage in practice.

The teaching of EP-A 639 598, too, is based on the polyaddition reaction of uretdione-functional polyisocyanates with diols and/or bifunctional chain
20 extenders and, as is evident from the examples, with monoalcohols. Even the use of isocyanurate-functional polyisocyanate-uretdiones having more than two NCO functions does not - owing to the use of monoalcohols - lead to more highly functional polyaddition products, the crosslinkers for PU powder coatings. However, as mentioned above, this is disadvantageous for the
25 quality of the coatings.

In accordance with DE-A-19 505 566, surprisingly, it was possible for the first time to use polyols having more than two hydroxyl groups to prepare the claimed uretdione-functional polyisocyanates. To do this, however, it was
30 first of all necessary partly to block the isocyanate groups of the polyisocyanate-uretdiones, in order to avoid gelling. On economic grounds, re-eliminable blocking agents were employed. However, this constitutes an ecological disadvantage.

The object of the present invention, therefore, was to provide uretdione-functional polyisocyanates, in order to use these crosslinkers to prepare PU polymers, in particular ecologically useful PU powder coatings, which are free from elimination products, and the PU powder coatings produced
5 accordingly which no longer have the abovementioned disadvantages of the prior art.

This object has been achieved in accordance with the claims.

10 The present invention accordingly provides hydroxyl- and uretdione-functional polyisocyanates essentially comprising

- A) from 55 to 86% by weight of uretdione,
- B) from 1.5 to 15% by weight of polyol with ≥ 3 hydroxyl groups, and
- 15 C) from 7.0 to 30% by weight of diol,

the polyaddition products carrying terminal hydroxyl groups and having a functionality of > 2 to < 3 , preferably between 2.1 and 2.9, molar masses of between 1600 and 15,000, preferably between 1900 and 10,000, and a free
20 isocyanate content of $< 0.5\%$ by weight.

The invention additionally provides for the use of the hydroxyl- and uretdione-functional polyisocyanates for preparing PU polymers, especially in combination with hydroxyl-containing polymers, in transparent and pigmented PU powder coatings which are free from elimination products and are
25 of increased network density, very good reactivity and excellent gloss, and provides transparent and pigmented PU powder coatings which are free from elimination products and comprise the novel hydroxyl- and uretdione-functional polyisocyanates having a functionality of > 2 to < 3 .

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The uretdiones (component A) employed in accordance with the invention are obtained from diisocyanates by known methods, and in principle it is possible to employ all known diisocyanates.

Preferred uretdiones, however, are derived from the diisocyanates selected from the group consisting of hexamethylene diisocyanate (HDI), 2-methylpentamethylene 1,5-diisocyanate (DI 51), 2,2,4(2,4,4)-trimethylhexamethylene diisocyanate and isophorone diisocyanate (IPDI), which
5 isocyanates can be employed individually or in mixtures as component A.

Particular preference is given to the use of the uretdione of isophorone diisocyanate.

10 The isocyanurate-free uretdione of isophorone diisocyanate has a high viscosity at room temperature of more than 10^6 mPa·s; at 60°C the viscosity is $13 \cdot 10^3$ mPa·s and at 80°C it is $1.4 \cdot 10^3$ mPa·s. The free NCO content is between 16.8 and 18.5% by weight; in other words, more or less high proportions of the polyuretdione of IPDI must be present in the reaction
15 product. The monomer content is $\approx 1\%$ by weight. The overall NCO content of the reaction product after heating at 180 - 200°C is 37.4 - 37.8% by weight.

The dimerization of aliphatic diisocyanates using conventional processes
20 and catalysts produces, as a byproduct, varying amounts of isocyanurate, so that the NCO functionality of the isocyanurate-containing polyisocyanate-uretdiones employed is from > 2 to 2.5. As a result it was very surprising that such isocyanurate-containing polyisocyanate-uretdiones could be used for the synthesis of hydroxyl- and uretdione-functional polyisocyanates having
25 a functionality of from > 2 to < 3 without the occurrence of gelling.

Suitable polyols (component B) in accordance with the invention are glycerol, trimethylolpropane, ditrimethylolpropane, trimethylolethane, 1,2,6-hexanetriol, 1,2,4-butanetriol, tris(β -hydroxyethyl)isocyanurate, penta-
30 erythritol, mannitol or sorbitol, with preference being given to the use of trimethylolethane, trimethylolpropane (TMP) and trishydroxyethyl isocyanurate (THEIC). They are used individually or in mixtures.

The diols (component C) employed in accordance with the invention include

all those which are commonly employed in PU chemistry; particular preference is given to ethylene glycol (E), triethylene glycol (TEG), 1,4-butanediol (B), 1,5-pentanediol (P), 1,6-hexanediol (HD), 3-methyl-1,5-pentanediol (Pm), neopentylglycol (N), 2,2,4(2,4,4)-trimethylhexanediol (T) and neopentylglycol hydroxypivalate (Eg).

The novel polyisocyanates advantageously also comprise chain extenders (component D) having a functionality of from ≥ 2 to ≤ 6 , in particular ≥ 2 to ≤ 4 , in the form of linear and/or branched hydroxyl-containing polyesters and/or polycaprolactones having a molar mass of between 180 and 2000, preferably between 230 and 1500, and hydroxyl numbers of between 900 and 50 mg of KOH/g, preferably between 700 and 100 mg of KOH/g. They are prepared, for example, by the condensation of polyols or diols and dicarboxylic acids.

Preferred chain extenders employed are linear hydroxyl-containing polycaprolactones having a molar mass of between 180 and 2000 and a hydroxyl number of between 625 and 50 mg of KOH/g.

Further preferred chain extenders used are branched polyesters or polycaprolactones having a functionality ≥ 3 , a molar mass of between 210 and 2000 and a hydroxyl number of between 900 and 100 mg of KOH/g.

The chain extenders are prepared using, preferably, the abovementioned polyols and/or diols, supplemented by 2-methyl-1,3-propanediol, diethylene glycol, 1,12-dodecanediol and also trans- and cis-cyclohexanedimethanol (CHDM).

The preferred dicarboxylic acids include aliphatic acids with or without alkyl branching, such as succinic, adipic (As), suberic, azelaic and sebacic acid (Sb), and 2,2,4-(2,4,4)-trimethyladipic acid; also covered by this definition are lactones and hydroxycarboxylic acids, such as ϵ -caprolactone and hydroxycaproic acid.

The novel hydroxyl-containing reaction products - components B, C and D - are employed such that the mixtures must include at least 1 mol of B and/or D having three or more OH groups in the OH mixture.

- 5 The novel mixing ratio of the hydroxyl-containing reactants to the uretdione must be chosen such that the functionality of the hydroxyl- and uretdione-functional polyisocyanates is between > 2 and < 3 .

The novel polyaddition products can be obtained, inter alia, by the process
10 described below.

Reaction in solvent generally takes place at temperatures from 50 to 100°C, preferably between 60 and 90°C. The OH component, polyol and/or diol and/or chain extender, is introduced as initial charge and the uretdione is
15 added as rapidly as possible but without the reaction temperature surpassing the abovementioned limits. The reaction is over after from 30 to 150 minutes. Subsequently, the solvent is removed. Apparatus suitable for this purpose comprises evaporating screws, filmtruders or else spray-driers.

20 Suitable solvents are benzene, toluene or other aromatic and/or aliphatic hydrocarbons, acetates, such as ethyl acetate or butyl acetate, and also ketones, such as acetone, methyl ethyl ketone and methyl isobutyl ketone, or chlorinated aromatic and aliphatic hydrocarbons, and also any desired mixtures of these or other inert solvents.

25

The invention also provides the solvent-free and continuous preparation of the process products by means of thorough kneading in a single- or multiscrew extruder, especially in a twin-screw extruder. The solvent-free synthesis requires temperatures from ≥ 110 to 190°C. It was surprising that
30 it is possible to employ such high temperatures for the uretdione syntheses. Such temperatures are already well within the range in which uretdiones unblock, so that high free isocyanate contents may result and hence uncontrolled reaction processes would be expected. This fact was significant for the synthesis of the hydroxyl-containing uretdione polyaddition product,

and it was all the more surprising that it could be realized. In this context, the short reaction times of < 5 minutes, preferably < 3 minutes, in particular < 2 minutes, proved to be advantageous.

- 5 It is also a matter of principle that the brief thermal exposure is sufficient to provide for homogeneous mixing of the reactants and, at the same time, for their complete or substantial reaction. Subsequently, controlled cooling is carried out in accordance with the establishment of equilibrium, and, if necessary, conversion is completed.

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- The reaction products are supplied to the kneading apparatus in separate product streams, it being possible to preheat the starting components to 120°C, preferably to 90°C. Where there are more than two product streams, they can also be metered in in clusters. Polyol and/or diol and/or chain
15 extender and/or catalysts and/or further customary coatings additives, such as leveling agents and/or stabilizers, can be combined into one product stream; the same applies to those which are inert toward isocyanate groups: catalysts and corresponding abovementioned coatings additives.

- 20 Similarly, the sequence of the product streams can be varied, and the entry point of the product streams may be different.

For afterreaction, cooling, comminution and bagging, known techniques and technologies are employed.

25

- To accelerate the polyaddition reaction it is also possible to use the catalysts which are customary in PU chemistry. They are employed in a concentration of from 0.01 to 1% by weight, preferably 0.03 to 0.5% by weight, based on the reaction components used. Tin(II) and (IV) compounds have proven
30 particularly suitable to date. Among these, particular mention is made of dibutyltin dilaurate (DBTL). However, other catalysts should not immediately be regarded as unsuitable.

The present invention provides, furthermore, for the use of the hydroxyl- and

uretdione-functional polyisocyanates for preparing polyurethane polymers, especially in combination with hydroxyl-containing polymers and/or with the additives customary in PU chemistry, for preparing transparent and pigmented PU powder coatings which are free from elimination products, have very good reactivity and are therefore economically and ecologically significant, and, surprisingly, possess excellent flexibility despite an increased network density.

The present invention also provides PU powder coatings which are free from elimination products, consisting of the novel polyisocyanates in combination with hydroxyl-containing polymers. Suitable reactants for PU powder coatings are compounds which carry those functional groups which, during the curing process, react with isocyanate groups as a function of temperature and time, examples being hydroxyl, carboxyl, mercapto, amino, urethane and (thio)urea groups. Polymers which can be employed are addition polymers, condensation polymers and polyaddition compounds.

In principle it is possible to use any polymer which contains more than two OH groups and melts at at least 70°C. These are polyetherpolyols, polyesteramidepolyols, polyurethanepolyols, hydroxylated acrylate resins, etc., whose OH groups are intended for crosslinking with the novel, uretdione-functional polyisocyanates. Among the numerous possibilities for hydroxyl-containing polymers within the framework of the invention, particular preference is given to polyesterpolyols. The hydroxyl-containing polyesters which are employed with particular preference have an OH functionality of > 2, an OH number of from 20 to 200 mg of KOH/g, preferably 30 to 150 mg of KOH/g, a viscosity of < 60,000 mPa·s, preferably < 40,000 mPa·s, at 160°C, and a melting point of from > 70 to ≤ 120°C, preferably from 75 to 100°C.

Polyesters of this kind can be obtained in a manner known per se by condensation in an inert-gas atmosphere at temperatures of from 100 to 260°C, preferably 130 to 220°C, in the melt or in an azeotropic procedure, as is described in Methoden der Organischen Chemie (Houben-Weyl), Vol.

14/2, 1 - 5, 21 - 23, 40 - 44, Georg Thieme Verlag, Stuttgart, 1963, or in C.R. Martens, Alkyd Resins, 51 - 59, Reinhold Plastics Appl. Series, Reinhold Publishing Comp., New York and in DE-A-19 57 483, 25 42 191, 30 04 876 and 31 43 060.

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The mixing ratio of the hydroxyl-containing polymers and the novel polyisocyanates is generally chosen such that there is 0.5 - 1.2, preferably 0.8 - 1.1, very preferably 1.0 NCO group per OH group.

10 In order to increase the rate of gelling of the heat-curable powder coatings it is possible to add catalysts. Catalysts used are organotin compounds such as dibutyltin dilaurate (DBTL), Sn(II) octoate, dibutyltin maleate, etc. The amount of catalyst added is 0.1 - 5 parts by weight per 100 parts by weight of the hydroxyl-containing polyester.

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To prepare PU powder coatings, the isocyanate component is mixed with the appropriate hydroxyl-containing polymer and, if desired, with catalysts and pigments and with customary auxiliaries, such as fillers and leveling agents, such as silicone oil and acrylate resins, and the mixture is homogenized in the melt. This can be done in suitable equipment, for example heatable kneading apparatus, but preferably by extrusion, in the course of which upper temperature limits of 130 to 140°C should not be exceeded. The extruded mass is cooled to room temperature, is comminuted suitably, and is then ground into the ready-to-spray powder. The ready-to-spray powder can be applied to appropriate substrates in accordance with the known methods, for example by electrostatic powder spraying, fluidized-bed sintering, or electrostatic fluidized-bed sintering. Following the application of the powder, the coated workpieces are cured by heating them at a temperature of from 150 to 220°C for from 60 to 4 minutes, preferably at from 160 to 200°C for from 30 to 6 minutes.

In the text below the subject-matter of the invention is illustrated in more detail with reference to examples.

The abbreviations used are explained in the description at the appropriate points (pages 3 to 4).

5 A Preparation of the novel hydroxyl- and uretdione-functional polyisocyanates

A1 Polyol chain extenders

General preparation procedure

10

The starting components - cf. Tables 1 and 2 - are placed in a reactor and are heated to $\approx 140^{\circ}\text{C}$ with the aid of an oil bath. After the substances have for the most part melted, 0.1% by weight of di-n-butyltin oxide is added as catalyst. Initial elimination of water takes place at from 150 to 160°C . Over
15 the course of 2 to 3 hours the temperature is raised from 180 to 190°C , and esterification is completed over the course of a further 8 to 10 hours. Throughout the reaction period, the bottom product is stirred and a gentle stream of nitrogen is passed through the reaction product. The acid number of the polyesters was always < 2 mg of KOH/g.

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A 1.1

Table 1: Polyol chain extenders (component D) - A 1.1; functionality: F = 2

Example A 1.1	Starting components in mol				Characteristics	
	As	Sb	N	P	HD	
1	-	-	2	-	-	OH number [mg of KOH/g]
2	-	1	2	-	-	viscosity at 25°C [mPa.s]
3	polycaprolactones from Interlox - Capa 200				335 ± 15	≈ 1500
4	polycaprolactones from Interlox - Capa 210				289 ± 10	≈ 1150
					216	melting range 18 - 23°C
					112	melting range 30 - 40°C

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A 1.2

Table 2: Polyol chain extenders (component D); functionality: F = > 3

Example A 1.2	Starting components in mol				Characteristics	
	As	N	HD	TMP	OH number [mg of KOH/g]	viscosity at 25°C [mPa.s]
1	2	1	1	1	270 ± 285	5500
2		polycaprolactones from Interlox - Capa 305			305 - 320	1350
3		polycaprolactones from Interlox - Capa 316			210 - 220	2300

A 2 Hydroxyl- and uretdione-functional polyisocyanates

General preparation procedures

5 A 2.1 From solvent

The polyol component - cf. Table 3 - and the catalyst (0.03 - 0.5% by weight of DBTL) are introduced as initial charge, dissolved in the solvent, to the reactor. With vigorous stirring and under an inert-gas atmosphere the
10 calculated amount of uretdione, dissolved in the solvent, is added at a rate such that the reaction temperature does not exceed 100°C. The reaction is monitored by means of titrimetric NCO determination and is over after 1 to 3 hours. The solvent is subsequently removed and the product is cooled and, if appropriate, comminuted.

15

A 2.2 Without solvent

The uretdione was fed, at a temperature of from 60 to 110°C, into the intake barrel of a twin-screw extruder, the polyol component - cf. Table 3 - being
20 metered in simultaneously at a temperature of from 25 to 110°C. The uretdione and/or the polyol component contained, if appropriate, the required amount of catalyst: from 0.03 to 0.5% by weight of DBTL, based on the end product.

25 The extruder employed is composed of ten barrels, of which five are heating zones. The temperatures of the heating zones cover a wide range - between 50 and 190°C - and can be controlled individually. All temperatures are setpoint temperatures; regulation within the barrels is accomplished by means of electrical heating and pneumatic cooling. The die element is
30 heated by means of an oil thermostat. The rotary speed of the twin screw, fitted with conveying elements, was between 50 and 380 rpm.

The reaction product, obtained at a rate of from 10 to 130 kg/h, is either cooled and then comminuted or shaped and bagged, or the melt itself is

shaped, cooled and bagged.

The physical and chemical characteristics of the novel process products, and the molar compositions, are summarized in Tables 3 to 5.

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The uretdiones, prepared by known processes, had the following characteristics:

IPDI uretdione

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free NCO: from 16.8 to 18.5% by weight

total NCO: from 37.4 to 37.8% by weight

DI 51 uretdione

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free NCO: from 20.1 to 21.2% by weight

total NCO: from 43.7 to 44.9% by weight

HDI uretdione (DESMODUR® N 3400)

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free NCO: from 20.9 to 22.1% by weight

total NCO: from 35.6 to 36.5% by weight

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Table 3: Hydroxyl- and uretdione-functional polyisocyanates

Example A 2	Composition in mol					Chemical and physical characteristics		
	uretdione comp. A	polyol comp. B	diol(s) comp. C	chain extender component D		NCO content [% by wt.]	melting range [°C]	glass transition temperature [°C]
	IPDI			F = 2	F = 3			
1	3.1	TMP (1)	E (2.6)	A 1.1.3 (0.5)	-	0	85-88	49-58
2	3.2	TMP (1)	E (2.7)	A 1.1.3 (0.5)	-	0	90-91	53-67
3	4	TMP (1)	B (3.5)	A 1.1.1 (0.5)	-	0	100-105	58-71
4	6	TMP (1)	E (5)	A 1.1.2 (1)	-	0	93-97	55-67
5	8	TMP (1)	HD (7)	A 1.1.3 (1)	-	0	94-97	59-69
6	9	TMP (1)	B (9)	-	-	0	135-138	99-115
7	9	TMP (1)	Pm (9)	-	-	0	123-126	96-108
8	9	TMP (1)	HD (9)	-	-	0	120-123	96-110
9	9	TMP (1)	T (9)	-	-	0	116-119	90-101
10	9	TMP (1)	Eg (9)	-	-	0	113-116	89-107
11	9	TMP (1)	B (5) Pm (4)	-	-	0	126-129	97-112

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Table 3: continued

Example A 2	Composition in mol					Chemical and physical characteristics			
	urethane comp. A	polyol comp. B	diol(s) comp. C	chain extender component D		NCO content [% by wt.]		melting range [°C]	glass transition temperature [°C]
	IPDI			F = 2	F = 3	free	total		
12	9	TMP (1)	B (4)	A 1.1.1 (2)	-	0	12.5	117-120	78-101
13	9	TMP (1)	B (7)	A 1.1.3 (2)	-	0	11.7	98-104	51-69
14	10	TMP (1)	B (8.5)	A 1.1.3 (1.5)	-	0	12.5	106-109	67-86
15	10	TMP (1)	B (7.5)	A 1.1.3 (2.5)	-	0	11.6	93-96	56-71
16	11	TMP (1)	B (9.5)	A 1.1.1 (1.5)	-	0	13.4	120-123	91-107
17	11	TMP (1)	B (4)	A 1.1.1 (7)	-	0	11.2	91-94	53-69
18	11	TMP (1)	B (9)	A 1.1.3 (2)	-	0	12.4	91-94	45-63

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Table 4: Hydroxyl- and uretdione-functional polyisocyanates

Example	Composition in mol					Chemical and physical characteristics			
	uretdione comp. A	polyol comp. B	diol(s) comp. C	chain extender component D		NCO content [% by wt.]	melting range [°C]	glass transition temperature [°C]	
	IPDI			F = 2	F = 3				
1	4	-	E (4)	-	A 1.2.2 (1)	0	98-101	55-68	
2	6	-	Pm (6)	-	A 1.2.2 (1)	0	105-109	57-71	
3	6	-	E (5)	A 1.1.1 (1)	A 1.2.2 (1)	0	97-100	56-67	
4	6	-	E (6)	-	A 1.2.3 (1)	0	95-97	50-70	
5	7	-	B (7)	-	A 1.2.3 (1)	0	93-96	48-69	
6	7	-	B (7)	-	A 1.2.2 (1)	0	105-108	77-91	
7	7	-	B (6)	A 1.1.1 (1)	A 1.2.2 (1)	0	91-95	48-65	
8	8	-	B (7)	A 1.1.3 (1)	A 1.2.1 (1)	0	73-76	21-41	
9	8	-	B (6)	A 1.1.1 (2)	A 1.2.3 (1)	0	91-94	47-69	
10	9	-	B (8)	A 1.1.1 (1)	A 1.2.2 (1)	0	106-109	75-92	

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Table 4: continued

Example A 2	Composition in mol					Chemical and physical characteristics			
	urethane comp. A IPDI	polyol comp. B	diol(s) comp. C	chain extender component D		NCO content [% by wt.]	melting range [°C]	glass transition temperature [°C]	
				F = 2	F = 3				
11	9	-	B (7.5)	A 1.1.3 (1.5)	A 1.2.2 (1)	0	93-96	59-77	
12	9	-	E (8)	A 1.1.4 (1)	A 1.2.2 (1)	0	83-88	44-55	
13	9	-	HD (8)	A 1.1.1 (1)	A 1.2.2 (1)	0	99-104	57-72	
14	10	-	Pm (8)	A 1.1.3 (2)	A 1.2.2 (1)	0	98-101	53-70	
15	10	-	B (7.5)	A 1.1.3 (2.5)	A 1.2.1 (1)	0	86-89	49-64	
16	10	-	B (3)	A 1.1.1 (7)	A 1.2.1 (1)	0	73-76	41-55	
17	10	-	P (6.75) B (2)	A 1.1.1 (1.25)	A 1.2.2 (1)	0	110-113	84-102	
18	11	-	B (10)	A 1.1.3 (1)	A 1.2.2 (1)	0	87-90	51-66	
19	11	-	B (8.5)	A 1.1.3 (2.5)	A 1.2.2 (1)	0	83-86	44-58	
20	12	-	B (7)	A 1.1.1 (5)	A 1.2.3 (1)	0	93-96	57-70	

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Table 5: Hydroxyl- and uretdione-functional polyisocyanates

Example	Composition in mol					Chemical and physical characteristics			
	uretdione comp. A	polyol comp. B	diol(s) comp. C	chain extender component D		NCO content [% by wt.]	melting range [°C]	glass transition temperature [°C]	
				F = 2	F = 3				
A 2	IPDI/HDI 5:1					free	total		
	1	5.5	0.5	TMP (1)	E (5)	A 1.1.2 (1)	-		
	2	7.5	1.5	TMP (1)	B (7)	A 1.1.1 (2)	-		
	3	9	1	TMP (1)	P (6.75) B (2)	A 1.1.1 (1.25)	-		
	4	8	2		Pm (9)	A 1.1.3 (1)	A 1.2.2 (1)		
5	10	1	TMP (1)	B (9)	A 1.1.3 (2)	-			
	IPDI/HDI								
6	6.5	0.5	-	B (7)	-	A 1.2.2 (1)			
7	8	1	-	B (8)	A 1.1.1 (1)	A 1.2.2 (1)			
8	9	1	TMP (1)	B (8.5)	A 1.1.3 (1.5)	-			

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B Polyesters

Table 6 below gives an overview of the polyesters obtainable commercially for formulating PU powder coatings.

5 Table 6

Example B	Manufacturer Country	Name	Chemical and physical characteristics			
			OH number [mg of KOH/g]	acid number [mg of KOH/g]	melting range [°C]	glass transition temperature [°C]
1	Hoechst AG Italy	ALFTALAT AN 739	55 - 60	2 - 4	82 - 90	> 50
2	DSM Netherlands	URALAC P 1460	38 - 41	4 - 4.5	70 - 75	50
3	UCB Belgium	CRYLCOAT 2392	27 - 33	2 - 3	85 - 100	> 50
						viscosity at 160°C [mPa.s]
						24 - 29.000
						40.000
						~ 35.000

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C Polyurethane powder coatingsGeneral preparation procedure

- 5 The comminuted products - uretdione-functional polyisocyanates (crosslinkers), polyesters, leveling agent masterbatch and, if appropriate, catalyst masterbatch - are intimately mixed together, if desired, with the white pigment in an edge runner mill and then are homogenized in an extruder at not more than 130°C. After cooling, the extrudate is fractionated and ground
- 10 to a particle size < 100 µm using a pin mill. The powder thus prepared is applied to degreased and optionally pretreated iron panels using an electrostatic powder spraying unit at 60 kV, and the panels are baked in a convection drying oven at temperatures between 170 and 200°C.

15 Leveling agent masterbatch

10% by weight of the leveling agent - a commercially available copolymer of butyl acrylate and 2-ethylhexyl acrylate - in the corresponding polyester are homogenized in the melt and, after solidifying, are comminuted.

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Catalyst masterbatch

5% by weight of a catalyst - DBTL - in the corresponding polyester are homogenized in the melt and, after solidifying, are comminuted.

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The abbreviations in the tables below denote:

LT	= layer thickness in µm	
EI	= Erichsen indentation in mm	(DIN 53 156)
30 CH	= crosshatch test	(DIN 53 151)
GG 60°	= Gardner gloss	(ASTM-D 5233)
Imp.rev.	= impact reverse in g·m	
HK	= König hardness in sec	(DIN 53 157)

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C 1 Pigmented powder coatings

Table 7:

Example C1 Formulation	1	2	3 ^{a)}	4	5	6	7	8	9	10	11	12
Crosslinker A 2	21.24	24.93	20.99	15.26	22.17	17.62	13.77	22.36	21.23	27.58	26.27	16.19
Table 3 Ex. 0	(4)	(6)	(6)	(6)	(9)	(10)	(12)	(13)	(14)	(16)	(18)	(18)
Polyester B 1	72.76	75.07	79.01	-	-	-	-	-	-	72.42	73.73	-
Polyester B 2	-	-	-	-	77.83	-	-	77.64	78.77	-	-	-
Polyester B 3	-	-	-	84.74	-	82.38	86.23	-	-	-	-	83.81
Notes	All formulations contain 40% by weight of TiO ₂ (white pigment) and 0.5% by weight each of leveling agent and benzoin, and also 0.15% by weight of DBTL; the OH/NCO ratio is 1.1; a) OH/NCO = 1.0.8											
Coatings data												
LT	64.79	59.67	63.70	65.76	58.70	56.63	67.79	61.72	54.72	79.99	70.85	61.90
GC 60°C	89.90	90	90	90.91	88.89	87.89	89/90	88.90	91	91	91	90.91
CH	0	0	0	0	0	0	0	0	0	0	0	0
El	9.7/10	> 10	> 10	> 10	9.7/10	> 10	9.6/9.9	> 10	9.3/10	> 10	> 10	9.1/10
Imp rev.	576	> 944.6	806.4	> 944.6	806.4	691.2	576	806.4	460.8	576	691.2	460.8
Notes	Curing conditions: 200°C/8 to 10', 180°C/15' or 170°C/25'											

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C 1 Pigmented powder coatings

Table 8:

Example C1 Formulation	1	2	3	4	5	6"	7	8"	9	10	11	12"
Crosslinker A 2	18.16	27.75	22.66	24.29	16.28	13.48	22.81	19.12	28.47	16.41	27.07	22.90
Table 4 Ex 0	(3)	(6)	(6)	(8)	(10)	(10)	(11)	(11)	(17)	(17)	(18)	(18)
Polyester B 1	-	72.25	-	-	-	-	-	-	71.53	-	72.93	77.1
Polyester B 2	-	-	77.34	75.71	-	-	77.19	80.88	-	-	-	-
Polyester B 3	81.84	-	-	-	83.72	86.52	-	-	-	83.59	-	-
Notes	All formulations contain 40% by weight of TiO ₂ (white pigment) and 0.5% by weight each of leveling agent and benzoin, and also 0.15% by weight of DBTL; the OH/NCO ratio is 1:1; q) OH/NCO = 1:0.8											
Coatings data												
LT	61-69	56-67	59-70	59-81	66-85	63-75	59-85	63-87	67-88	62-70	80-92	85-97
GG 60°-1	89	89-90	89	88/89	88-91	91/92	90-92	90-92	90-91	90-91	90-91	91
CH	0	0	0	0	0	0	0	0	0	0	0	0
EI	> 10	> 10	> 10	9.4/9.8	9.0/10	8.7/9.6	> 10	9.5/10	> 10	8.9/10	> 10	9.6/10
Imp.rev.	806.4	> 944.6	> 944.6	345.6	345.6	230.4	576	460.8	691.2	345.6	576	345.6
Notes	Curing conditions: 200°C/8 to 10', 180°C/15' or 170°C/25'											

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C 1 Pigmented powder coatings

Table 9:

Example C1 Formulation	1	2	3	4"	5	6	7	8	9	10
Crosslinker A 2	27.75	17.24	25.07	21.12	20.33	15.36	15.98	27.58	21.92	16.64
Table 5 Ex. 0	(1)	(1)	(3)	(3)	(3)	(3)	(5)	(7)	(8)	(8)
Polyester B 1	72.25	-	74.93	78.88	-	-	-	72.42	-	-
Polyester B 2	-	-	-	-	79.67	-	-	-	78.08	-
Polyester B 3	-	82.76	-	-	-	84.64	84.02	-	-	83.36
Notes	All formulations contain 40% by weight of TiO ₂ (white pigment) and 0.5% by weight each of leveling agent and benzoin, and also 0.15% by weight of DBTL; the OH/NCO ratio is 1:1; o) OH/NCO = 1:0.8									
Coatings data										
LT	65-82	71-89	72-89	69-90	67-92	81-93	67-85	63-81	77-91	67-80
GG 60°	89/90	90	89-90	90	89-90	90	89-91	90/91	90/91	89/91
CH	0	0	0	0	0	*	0	0	0	0
El	> 10	9.6/10	> 10	> 10	> 10	> 10	9.7/10	9.5/10	> 10	9.7/10
Imp. rev.	691.2	460.8	691.2	576	806.4	691.2	576	691.2	576	460.8
Notes	Curing conditions: 200°C/8 to 10'; 180°C/15'; or 170°C/25'									

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C 2 Transparent powder coatings

In accordance with the process described, transparent powder coatings as well were prepared, applied and baked at between 200 and 170°C.

Table 10:

[illegible]

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Claims:

1. A hydroxyl- and uretdione-functional polyisocyanate essentially comprising
- 5 A) from 55 to 86% by weight of uretdione
 B) from 1.5 to 15% by weight of polyol with ≥ 3 hydroxyl groups and
 C) from 7.0 to 30% by weight of diol
- 10 the polyisocyanate carrying terminal hydroxyl groups and having a functionality of > 2 to < 3 , a molar mass of between 1600 and 15,000, and a free isocyanate content of $< 0.5\%$ by weight.
- 15 2. A hydroxyl- and uretdione-functional polyisocyanate as claimed in claim 1, which additionally comprises
- D) from 5.5 to 33% by weight of chain extender having a functionality of ≥ 2 to ≤ 6 .
- 20 3. A hydroxyl- and uretdione-functional polyisocyanate as claimed in claim 1 or 2, which has a functionality of from 2.1 to 2.9 and a molar mass of between 1900 and 10,000.
- 25 4. A hydroxyl- and uretdione-functional polyisocyanate as claimed in any of claims 1 to 3, wherein uretdiones of the diisocyanates hexamethylene 1,6-diisocyanate, 2-methylpentamethylene 1,5-diisocyanate, 2,2,4(2,4,4)-trimethylhexamethylene diisocyanate or isophorone diisocyanate are employed, individually or in mixtures.
- 30 5. A hydroxyl- and uretdione-functional polyisocyanate as claimed in any of claims 1 to 4, wherein the polyol employed is glycerol, trimethylolpropane, ditrimethylolpropane, trimethylethane, 1,2,6-hexanetriol, 1,2,4-butanetriol, tris(β -hydroxyethyl) isocyanurate, pentaerythritol, mannitol or sorbitol.

6. A hydroxyl- and uretdione-functional polyisocyanate as claimed in any of claims 1 to 5, wherein the polyol employed is trimethylolethane, trimethylolpropane (TMP) and trishydroxyethyl isocyanurate (THEIC), individually or in mixtures.
- 5
7. A hydroxyl- and uretdione-functional polyisocyanate as claimed in any of claims 1 to 6, wherein the diols employed are ethylene glycol, triethylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, neopentylglycol, 2,2,4(2,4,4)-
- 10 trimethylhexanediol (isomer mixture) and neopentylglycol hydroxypivalate, individually or in mixtures.
8. A hydroxyl- and uretdione-functional polyisocyanate as claimed in any of claims 1 to 7, wherein the chain extenders employed are linear
- 15 and/or branched hydroxyl-containing polyesters or polycaprolactones having a molar mass of between 180 and 2000 and a hydroxyl number of between 900 and 50 mg of KOH/g.
9. A hydroxyl- and uretdione-functional polyisocyanate as claimed in any
- 20 of claims 1 to 8, wherein the chain extenders employed are linear hydroxyl-containing polyesters or polycaprolactones having a molar mass of between 180 and 2000 and a hydroxyl number of between 625 and 50 mg of KOH/g.
- 25 10. A hydroxyl- and uretdione-functional polyisocyanate as claimed in claim 8, wherein the chain extenders employed are branched polyesters or polycaprolactones having a functionality ≥ 3 , a molar mass of between 210 and 2000 and a hydroxyl number of between 900 and 100 mg of KOH/g.
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11. A hydroxyl- and uretdione-functional polyisocyanate as claimed in any of claims 8 to 10, wherein the hydroxyl-containing polyesters or polycaprolactones are built up from at least in each case one monomer selected from ethylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-

- hexanediol, 3-methyl-1,5-pentanediol, 2,2,4(2,4,4)-trimethylhexanediol, neopentylglycol hydroxypivalate, 2-methylpropanediol, 2,2-dimethylpropanediol, diethylene glycol, 1,12-dodecanediol, trans- and cis-cyclohexanedimethanol and at least in each case one monomer selected from succinic, adipic, suberic, azelaic, sebacic acid, 2,2,4(2,4,4)-trimethyladipic acid (isomer mixture), ϵ -caprolactone and hydroxycaproic acid.
12. A hydroxyl- and uredione-functional polyisocyanate as claimed in any of claims 8 to 11, wherein the chain extenders include not only the conventional carboxylic acids, hydroxycarboxylic acids or lactones but at least one mole of polyol selected from the group consisting of trimethylolethane, trimethylolpropane, trishydroxyethyl isocyanurate and pentaerythritol.
13. A hydroxyl- and uretdione-functional polyisocyanate as claimed in any of claims 8, 11 and 12, wherein chain extenders based on ϵ -caprolactone and/or hydroxycaproic acid are preferably employed.
14. A hydroxyl- and uretdione-functional polyisocyanate as claimed in any of claims 1 to 13, wherein chain extenders having a functionality of from ≥ 2 to ≤ 4 are employed.
15. A process for preparing a hydroxyl- and uretdione-functional polyisocyanate as claimed in any of claims 1 to 14, which comprises employing the hydroxyl-containing reactants B, C and D as mixtures, where at least one mole of B and/or of the chain extender D having more than two hydroxyl groups must be present in the mixture.
16. The process as claimed in claim 15, wherein the reaction of the starting products is carried out at from 50 to 100°C in a solvent which is removed after the reaction has been carried out.
17. The process as claimed in claim 15, wherein the reaction of the starting

products is carried out without solvent in an intensive kneading apparatus at temperatures of from 110 to 190°C.

- 5 18. The process as claimed in claim 17, wherein the reaction is carried out in a twin-screw extruder.
- 10 19. The process as claimed in any of claims 15 to 18, wherein the reaction is carried out using catalysts in a concentration of from 0.01 to 1% by weight, based on the starting materials employed.
- 20 20. The process as claimed in any of claims 15 to 19, wherein organotin compounds are employed as catalysts.
- 15 21. The process as claimed in any of claims 15 to 20, wherein from 0.03 to 0.5% by weight of catalysts is employed.
- 20 22. The use of a hydroxyl- and uretdione-functional polyisocyanate as claimed in any of claims 1 to 14, in combination with hydroxyl-containing polymers, for preparing transparent and pigmented polyurethane powder coatings which are free from elimination products and have a high network density.
- 25 23. A transparent or pigmented polyurethane powder coating which is free from elimination products, which comprises hydroxyl- and uretdione-functional polyisocyanates which are free from blocking agents and have a functionality of from > 2 to < 3 , as claimed in any of claims 1 to 14, in combination with hydroxyl-containing polymers and with further additives and auxiliaries.
- 30 24. A polyurethane powder coating as claimed in claim 23, which is based on an OH/NCO ratio of 1:0.5 to 1.2, preferably 1:0.8 to 1.1, in particular 1:1.
25. A polyurethane powder coating as claimed in claim 23 or 24, to which

catalysts are added in a concentration of from 0.03 to 0.5% by weight, including the amount of catalyst already present from the hydroxyl- and uretdione-functional polyisocyanates.

- 5 26. A polyurethane powder coating as claimed in any of claims 23 to 25, to which organotin compounds are added as catalysts.
27. A polyurethane powder coating as claimed in any of claims 23 to 26, with which from 0.05 to 0.15% by weight of catalysts is employed.
- 10 28. A polyurethane powder coating as claimed in any of claims 23 to 27, wherein the hydroxyl-containing polymers employed are polyesters having a functionality > 2 , an OH number of from 20 to 200 mg of KOH/g, a viscosity $< 60,000$ mPa·s at 160°C , and a melting point $\geq 70^{\circ}\text{C}$ and $\leq 120^{\circ}\text{C}$.
- 15 29. A polyurethane powder coating as claimed in any of claims 23 to 28, wherein the hydroxyl-containing polymers employed are polyesters having a functionality > 2 , an OH number of from 30 to 150 mg of KOH/g, a viscosity $< 40,000$ mPa·s at 160°C , and a melting point of from 75°C to $\leq 100^{\circ}\text{C}$.
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